

1. Abstract

Development of a Method for In Situ Measurement of Perchlorate

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2. Introduction.

Why Should Perchlorate be Monitored?

- Perchlorate is a known contaminant of certain water supplies.
- Perchlorate has known toxicity to the thyroid gland.
- Perchlorate in water supplies is regulated in several states and is on the EPA's Contaminant Candidate List.
- Remediation methods are under development -- no single method reduces perchlorate below toxic levels.
- On-site monitoring methods are needed to verify and control remediation.
- The portable perchlorate sensor developed by IA, Inc. can fulfill monitoring needs.

The concept of the technology.

The perchlorate sensor (patent pending) uses ion chromatography (IC) along with a proprietary ion selective electrode (ISE) specific for perchlorate in place of a conductivity detector. Use of the ISE reduces the complexity of instrumentation by eliminating the need to suppress mobile phase conductivity and reduces the possibility of false positive results from unknown interfering anions. The small size of the ISE, along with improvements in IC, make the IC-ISE readily miniaturizable. This feature lends itself to field use and to installation in test wells. The following drawing (Figure 1) sketches the major systems in a cylindrical configuration.

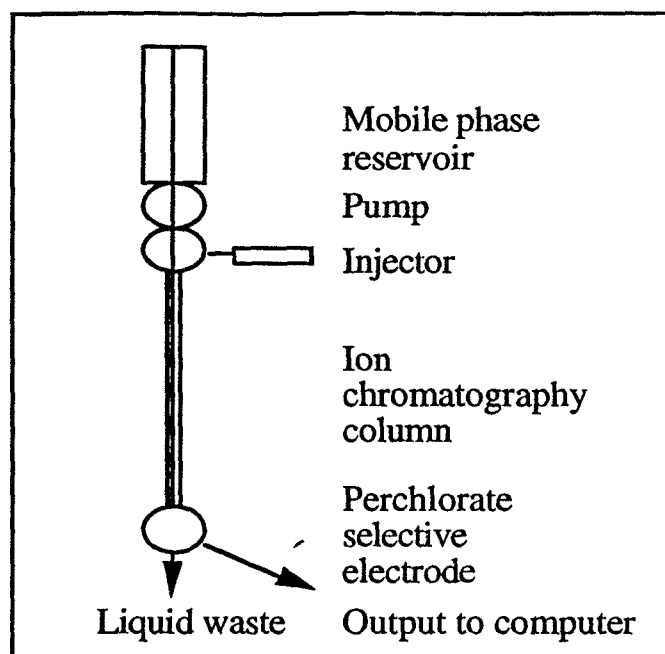


Figure 1: IA's proprietary perchlorate sensor.

Alternative technologies.

IA's proposed IC-ISE sensor offers the best near term, cost effective, practical solution to the need for a portable or *in situ* perchlorate monitoring technology. The proposed method is superior in these features to all competing technologies that meet the required detection limit: IC with suppressed conductivity, electrochromatography (based upon electroosmotic flow of the mobile phase) and an (as yet undiscovered) highly selective electrode for direct perchlorate sensing. Relevant characteristics of these methods are compared in Table 1.

Key Requirements	IA's technology	Standard method	Electroosmotic flow	Direct sensing
detect 2.5 ppb perchlorate*	yes	yes	yes	no
portable <i>in situ</i> capability	yes	no	yes	yes
proven selective for perchlorate	yes	yes	yes	no
based upon proven, robust technology	yes	yes	no	yes
capable of unattended, long term operation in the field	yes	no	no	yes

Table 1: Comparison of sensing technologies. Of available perchlorate sensing technologies, only IA's sensor meets all five key criteria for *in situ* monitoring. *in the presence of common interfering ions.

IC with measurement of suppressed conductivity is the current EPA standard method to detect ions at the ppb level and has been modified to detect as low as 1 ppb perchlorate. Since conductivity measurements are entirely non-selective, the only physical parameter by which an ion is identified is its chromatographic retention time. Because solution conductivity is non-selective this limitation is unlikely to be improved upon. Only the substitution of a more selective detection method for IC truly holds promise of improved fidelity in monitoring perchlorate.

3. Experimental methods, results and discussion.

Description of the perchlorate ISE

Electrode composition. The electrodes were prepared using the anion exchanger TOPB (tetraoctyl phosphonium bromide, high molecular weight poly(vinyl) chloride, and nitrophenyl octyl ether as the plasticizer. Flow through electrodes were prepared using narrow-bore PVC tubing (ID = 0.014 inches). The membrane cocktail was pipetted between proximal ends of tubing and was allowed to dry. To protect the sensing surface, each electrode was placed within a section of a 1000 μ L pipet tip, a length of stranded 24 ga. aluminum wire was inserted, the "inner" electrolyte solution was added and the pipet tip was sealed with epoxy potting compound.

Selectivity of the perchlorate ISE. Selectivity experiments were performed with the perchlorate ISE in quiescent solution. Responses were measured by the standard conductivity measurement (without the use of suppression), using a conductivity detector. As shown in Table 2, the conductivity detector is nonselective, giving a similar response for perchlorate and all the interfering anions tested. In contrast, the perchlorate ISE produced a much larger response to perchlorate than to all the interfering anions tested.

anion	Selectivity, $\text{ClO}_4 : x$	
	Conductivity	Perchlorate ISE
Cl^-	1.4	720
Br^-	0.2	500
SCN^-	1.1	770
NO_2^-	1.0	720
NO_3^-	7.3	280
PO_4^-	ND	630
CO_3^-	ND	670
SO_4^-	ND	> 1000
ClO_4^-	1.0	1.0

Table 2: The ISE provides 100 - 1000-fold selectivity over commonly occurring anions. Selectivity was determined by flow injection analysis using the perchlorate ISE, and was calculated from the response of each anion relative to response to perchlorate (ClO_4) at a range of anion concentrations. ND: not done.

The brassboard system.

The analytical system developed consists of an HPLC pump, injector, column, pH meter, strip chart recorder, reference electrode, and perchlorate specific electrodes, which occupies an area of about 2 feet by 2 feet of bench space. In the future prototype, the functions of the pH meter and chart recorder will be assumed by a digital interface. The standard HPLC pump will be replaced by a miniature pump, such as a solenoid, piston or positive displacement pump, which has an output of 200 - 300 psi. By these means, all the functions displayed on the benchtop system will become miniaturized and made suitable to place in a 2 inch test well. In addition, the miniaturized components can be rearranged for monitoring of surface water. Finally, the components can readily be reconfigured for placement within, or outside, a device or facility dedicated to perchlorate remediation.

Electrode storage conditions. A variety of experiments indicated that "preconditioning" of electrodes increases the response to low ppb levels of perchlorate. Since the ion exchanger, TOPB, is able to leach into the surrounding medium, it seems reasonable to provide a sufficient amount of the primary ion to complex much of the ionophore, thereby neutralizing the charge on the ionophore. This will make TOPB more hydrophobic and thus decrease its partition coefficient into water. We initiated a test of electrode storage conditions, using perchlorate ISEs that were stored overnight, first in the presence of 10 ppb perchlorate, then overnight in the absence of perchlorate, and finally overnight again in the presence of 10 ppb perchlorate. Electrodes were tested as detectors on the DEAE chromatography column, described below. The results of these experiments clearly showed that storage conditions are important (Figure 7). While the relative response to different levels of perchlorate in a sample did not change by much, absolute responses increased by about 20%.

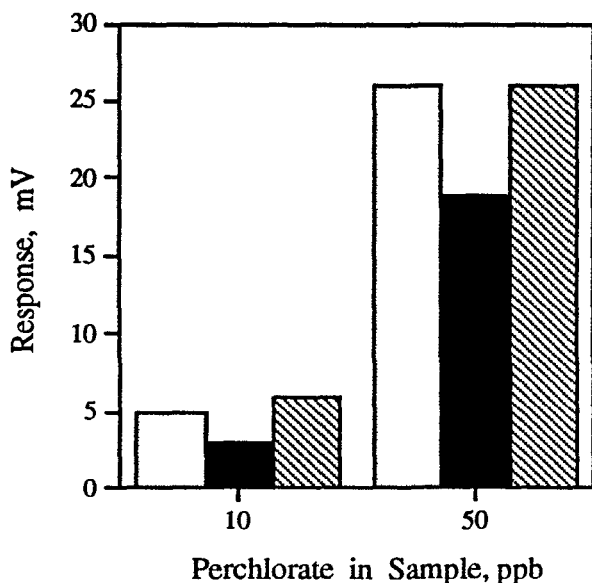


Figure 2. Test of electrode storage conditions. Electrodes were stored overnight, first in 0.2 mM Na₂SO₄ and 0.1 μM NH₄ClO₄ (light gray bars), followed by overnight in 0.2 mM Na₂SO₄, (dark), followed by overnight in 0.2 mM Na₂SO₄ and 0.1 μM NH₄ClO₄ (diagonal). The ISEs were used as detectors for the 1.1 x 100 mm DEAE column. Mobile phase: 0.2 mM Na₂SO₄, pH 4.5. Flow rate: 0.7 mL/min.

Reduction of column diameter. Reducing the volume of the stationary phase should result in lower dilution of the sample, with corresponding increases in response at the electrode (peak height), and

should reduce the retention factor for all anions. Thus, decreasing the diameter from 4.6 to 1.1 mm (both of which are standard column diameters) should result in about 15-fold increase in response, i.e., 15-fold reduction in the detection limit. We used the standard weak anion exchanger, DEAE silica, and prepared columns of varying diameter. Experiments with DEAE indicated that, as expected, both the retention factor and peak height are quite sensitive to the dimensions of the column (Table 3). Using the 8 mm column, neither perchlorate nor sulfate eluted within 15 min due to the high retention of the solute at the near-neutral pH of the mobile phase, but the other anions did elute. The 4.6 mm column gave similar relative retention, but each anion eluted about 3-fold faster, due to the significantly reduced volume (about 3-fold). In addition, peak heights improved considerably with reduced column size, illustrating the greater dilution a sample undergoes when injected onto a larger column.

anion	[anion], mM	column diameter (mm)					
		8			4.6		
		retention time (min)	retention factor (R_f)	peak height (mm)	retention time (min)	retention factor (R_f)	peak height (mm)
chloride (Cl^-)	16.8	5.7	1.7	10	1.9	0.6	106
bromide (Br^-)	20.0	7.6	2.6	6	2.1	0.8	100
iodide (I^-)	20.0	13.2	5.3	2	3.0	1.5	52
nitrite (NO_2^-)	20.0	7.2	2.4	6	2.1	0.8	98
nitrate (NO_3^-)	20.0	7.9	2.8	5	2.2	0.8	76
sulfate (SO_4^{2-})	20.0	N/A	N/A	N/A	3.8	2.2	43
perchlorate (ClO_4^-)	50.0	N/D	N/D	N/D	3.4	1.8	53

Table 3. Retention of anions on DEAE columns of 8 and 4.6 mm diameter. The columns were 150 mm long and either 8 mm (left) or 4.6 mm (right) in diameter. Injection volume: 0.25 mL; detector: conductivity (Anspec); mobile phase: 20 mM Na acetate pH 6.0; flow rate: 1 mL/min.

As the elution of perchlorate using a DEAE column of 4.6 mm diameter required a large retention time, we prepared a 1.1 x 100 mm column containing the DEAE exchanger. To further reduce the retention volume, we tested lowering the pH in the mobile phase, which should reduce the energy of interaction between DEAE and anions. Testing pH 4.5 and 3.0 indicated that the more acidic mobile phase reduced the retention factor for all anions (Figure 3).

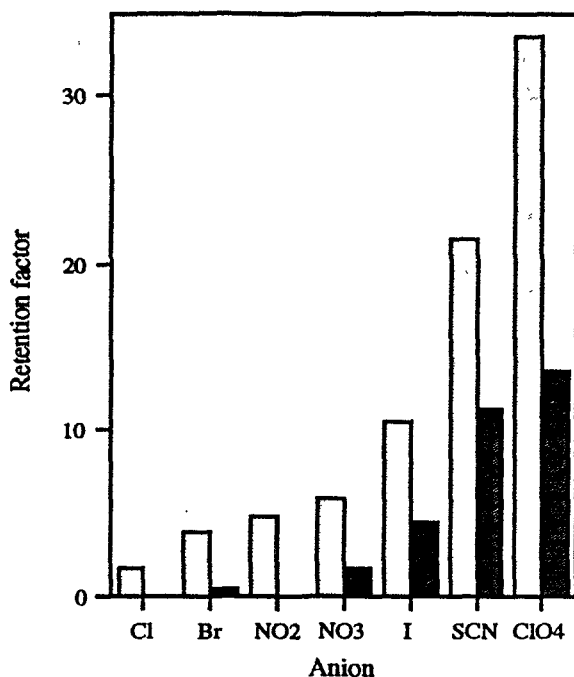


Figure 3. Reduction of pH in the mobile phase reduces retention factor on DEAE. Mobile phase: 20 mM Na₂SO₄, pH 4.5 (light bars) or pH 3.0 (dark). All anions at 2 mM, except perchlorate at 10 μ M. Injection volume 20 μ L. Flow rate: 1.0 mL/min.

Sample injection volume. Preliminary data demonstrated that the ISE can detect perchlorate at ~1 ppb when used without chromatography (equilibrium measurement). To improve the residence time of chromatographic peaks, we studied whether increasing sample volume would allow detection of low levels of perchlorate. The initial study showed that increasing the sample volume above some minimum gave proportional increases in detector response (Figure 4).

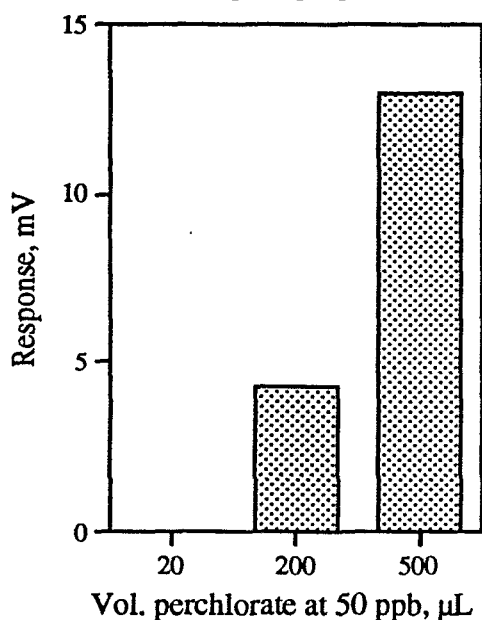


Figure 4. Increase in response with sample injection volume. Varying volumes of a 50 ppb ammonium perchlorate sample were injected, with mean peak heights at 200 and 500 μ L giving the same approximate ratio as the injected volume. In this experiment, the 20 μ L sample was not detectable above baseline noise. Mobile phase: 0.2 mM Na₂SO₄, pH 3. Stationary phase: DEAE, 1.1 x 100 mm. Flow rate: 0.7 mL/min.

Having demonstrated detectability of perchlorate with large sample volumes, we tested whether we could detect low ppb perchlorate. We injected 500 μ L of perchlorate at 10, 50 and 100 ppb and obtained responses which were approximately proportional to perchlorate concentration (Figure 5).

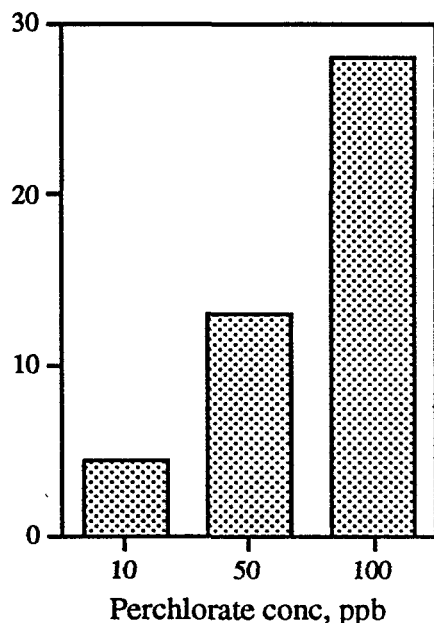


Figure 5. Response of the IC-ISE to varying concentrations of perchlorate. Injection volume: 500 μ L. Mobile phase: 0.2 mM Na_2SO_4 , pH 3. Stationary phase: DEAE, 1.1 x 100 mm. Flow rate: 0.7 mL/min.

Detection of perchlorate in the presence of other anions.

Since the ionic composition of water from various sources can range widely, we have used both buffered solutions and natural groundwater spiked with various levels of perchlorate to demonstrate that the IC-ISE detects perchlorate at or below the 18 ppb action level and in the presence of common anions. Figure 6 presents scans of chromatograms of samples composed of perchlorate at 10 and 18 ppb, along with varying levels of other anions. Perchlorate is the second peak in each run, eluting in about 8 minutes under those conditions. Adding sulfate or chloride up to about 1000 ppm had no measurable impact on the elution of perchlorate.

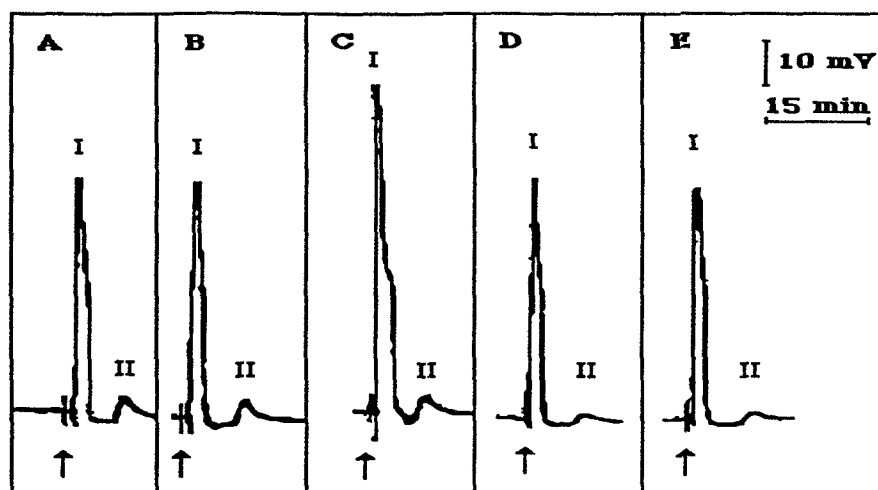


Figure 6: Measurement of low ppb perchlorate in buffered solutions. Interferents are in peak I and perchlorate in peak II in each chromatogram; arrows indicate injection. A: 18 ppb perchlorate, 192 ppm sulfate; B: 18 ppb perchlorate, 355 ppm chloride, 192 ppm sulfate; C: 18 ppb perchlorate, 1000 ppm chloride, 192 ppm sulfate; D and E: 10 ppb perchlorate, 355 ppm chloride, 192 ppm sulfate.

Measurement of perchlorate in groundwater samples. The measurement of perchlorate spiked into groundwater samples shows that the IC-ISE method works with water of largely unknown content. We obtained a sample of local well water (South Lyon, MI) and spiked it to 0, 2.5, 5, 10, 15 or 20 ppb perchlorate. The unspiked sample had a conductivity of $916 \mu\text{S}/\text{cm}$ with total dissolved solids of $449 \text{ mg}/\text{L}$. To demonstrate the performance of the IC-ISE technology, we analyzed groundwater samples that were spiked with various levels of perchlorate. Peak responses shown in Figure 7 are presented as a calibration curve in Figure 8. The IC-ISE gave a linear response to perchlorate concentration with an excellent correlation coefficient (Figure 8).

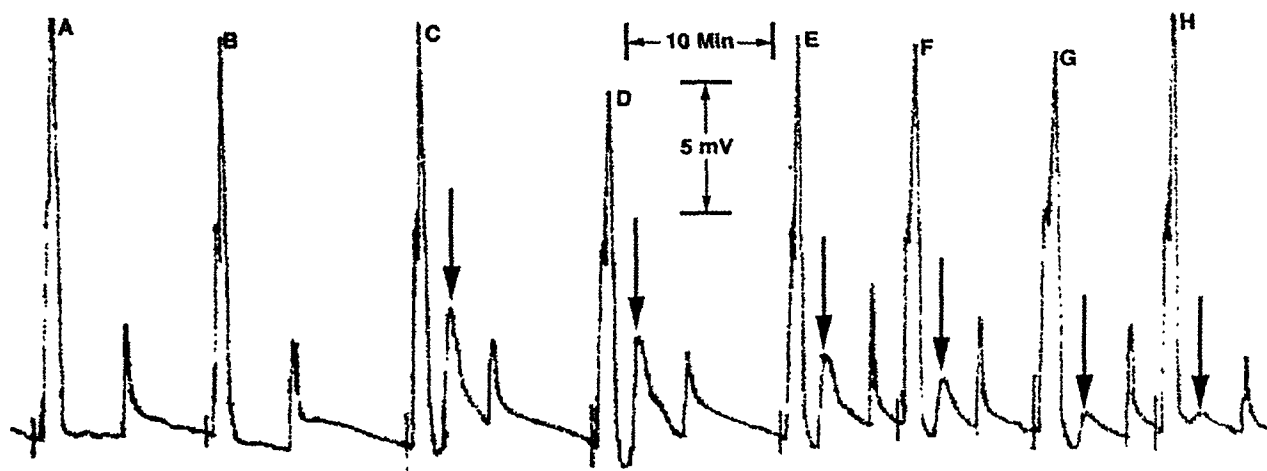


Figure 7: Response to perchlorate spiked into groundwater. A and B: 0; C and D: 20; E: 15; F: 10; G: 5; and H: 2.5 ppb.

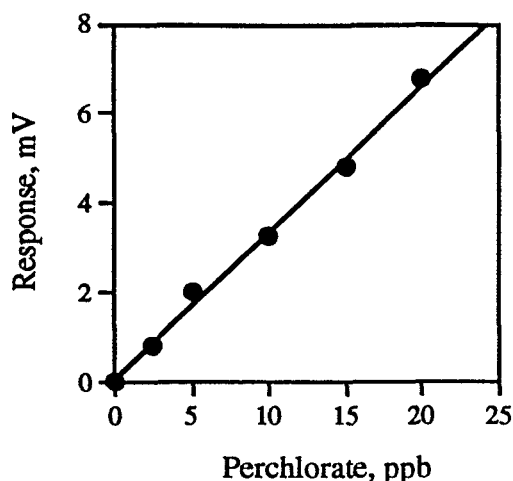


Figure 8: Calibration curve of perchlorate spiked into groundwater. Data in this graph were taken from the peak responses for each chromatogram in Figure 7. Equation of the linear regression line:

$$\text{Response (mV)} = 0.328[\text{perchlorate}] + 0.081$$

$$R^2 = 0.995$$

Reduction of system hydrostatic pressure.

As indicated above, typical HPLC pumps as used in the benchtop system provide hydrostatic pressures, up to about 3000 psi, that are required to push the mobile phase through the tightly-packed stationary phase. To reduce the requirement for a high pressure system we prepared a stationary phase comprised of larger particles (WP DEAM PrepHPL2 (Baker)). This allowed a reduction of system pressure from about 2200 psi to about 210 psi, and gave chromatograms that still showed good separation of perchlorate from anions in groundwater, and appear to result in similar sensitivity (Figure 9; compare to Figure 7). This material provides the flexibility in system design to use lower pressure pumps.

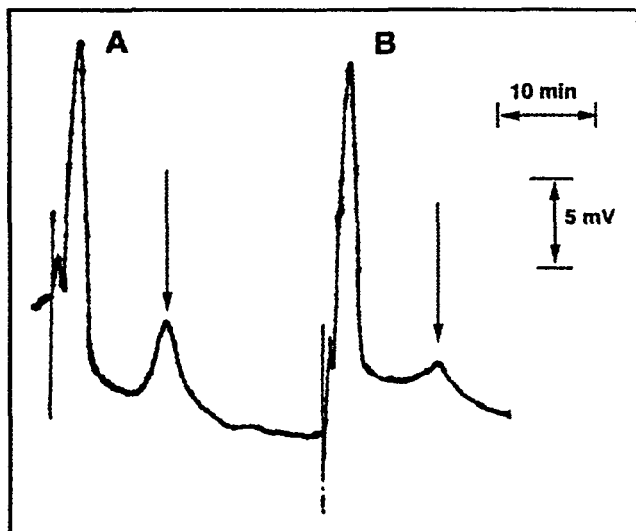


Figure 9. Chromatograms of perchlorate spiked into groundwater, with elution through a column prepared using WP DEAM PrepHPL2 (Baker). Chromatogram A has perchlorate at 20 ppb, and B is at 2.5 ppb (arrows).

Calibration curve for perchlorate in groundwater samples.

To verify that the IC-ISE responds with the new stationary phase as it did with the old one, we performed a series of chromatograms using natural groundwater spiked with perchlorate to levels

of 0, 2.5, 5, 10, 15 and 20 ppb. The measured peak responses fit well on a linear regression line (Figure 10).

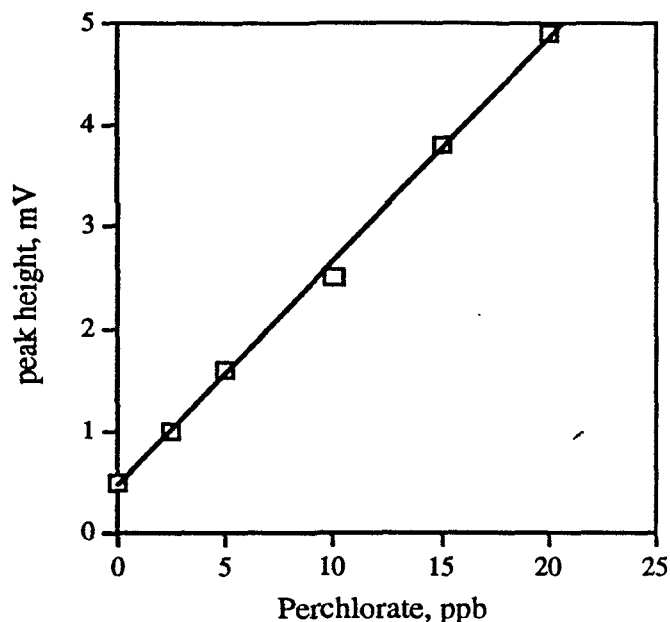


Figure 10. Calibration curve of perchlorate spiked into groundwater. Varying levels of perchlorate were added to untreated water obtained from a well in South Lyon, MI. Equation of the regression line:

$$\text{Response (mV)} = 0.22\{\text{perchlorate}\} + 0.456.$$

$$R^2 = 0.998.$$

4. Conclusions.

- The IC-ISE sensor provides a unique solution for perchlorate monitoring below the EPA action level.
- As a portable system, the IC-ISE lends itself to "down hole" and field monitoring.
- Since the IC-ISE uses simpler instrumentation and its operation can be easily automated, it can be adapted to remote monitoring of perchlorate remediation.
- IC-ISE is a flexible system and both analytical components can readily be modified to allow monitoring of other analytes.